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DEVELOPMENT OF HYDROCARBON ANALYSES AS A MEANS OF DETECTING LIFE IN SPACE

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SUMMARY

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Extensive data are being acquired on biological, sedimental, and abiotic alkanes. More than 300 GLC chromatographic "fingerprints", 100 mass spectra, and many infrared and ultraviolet spectra of naturally occurring hydrocarbons have been catalogued. These data indicate that biotic hydrocarbons are readily distinguishable from abiotic alkanes. Benzene extracts of elimination products and of Recent sediments contain comparable percentages of alkanes. These percentages usually exceed greatly the concentrations of alkanes in biological lipids but are significantly less than the concentrations of alkanes in ancient sediment extracts or crude oils. Paraffinic hydrocarbons from living things, fecal matter, and sediments have similar structures and optical properties. Analyses of alkanes of various geologic ages show that different types of biological alkanes can apparental keep their characteristics for more than a billion years in terrestrial environments.

Data gathered under NASw508 strongly support the hypothesis that saturated hydrocarbons are the best preserved and most widely distributed products of former organisms on earth. Alkanes may retain generally the most legible records of ancient life.

Author

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INTRODUCTION

Terrestrial sediments, glaciers, and bitumens contain fossils and remains of former life. Shells of marine organisms underlay most continental surfaces. Imprints of tropical-type ferns are embedded in Antarctican coals. Skeletons of dinosaurs and the frozen remains of mammoths tell of transitory existences of powerful animals on earth. Marked or, perhaps, catastrophic changes have altered the inhabitants, climates, and features of prehistoric worlds. Evidence of these changes are retained mainly in biological records, but the nature and scope of the events that caused these changes may not be determinable from terrestrial records alone.

Prebiotic materials, remnants of life and living things may be found on other celestial bodies. Biological explorations in space could reveal many secrets about the origins of life, the earth, and the solar system. Correlations and distributions of bilogical records on other planets may define the effects and frequencies of natural events which altered worlds. Knowledge of phenomena that have severely affected previous biota could be invaluable to man. Such knowledge may be the most important result to be obtained from the space effort.

Because biological explorations in space are expensive, methods are needed for a reliable assessment of whether or not a specific body has ever supported life. Public opinion almost certainly will favor the investigation of any planet where organisms have lived or do exist, but wasteful repeated explorations of barren bodies would be difficult to defend. Economic considerations recommend the use of a generally applicable means of detecting biological activity on other planets. Subsequent discussions will suggest why alkanes may be ubiquitous and dependable biological indicators which could be used in conjunction with other methods[1] in space explorations.

<u>Origin and Compositions of Alkanes</u>

During the last decade, much has been learned about the structures and functions of nucleic acids.[2,3] These acids transmit the genetic and enzymatic codes that ensure the continuity of the species and of life.[4] Both, the shapes of organisms and of the chemical constituents of living cells are apparently controlled by molecular "templates", and the controls exerted on biosynthetic products are remarkably restrictive.[4]

Plants and animals are composed of an infinitesimal fraction of the compounds that may be formed from carbon in combination with other elements. Similar or identical molecules occur in highly-ordered arrays in all living cells. Organic compounds are probably the most common heritage of life in general. The structures, distributions, and isotopic order displayed by certain biological molecules may provide a reliable means of distinguishing animate from inanimate matter, but only stable remnants of life can retain their identities.

Stability may be an inherent or an acquired property of organic substances. Legible records of ancient organisms persist chiefly in their mineralized (fossil) and preserved (molecular) remnants. Fossils have been utilized for many years in paleobiological investigations, and modern analytical techniques are making it possible to use stable organic molecules as well. Alkanes are apparently the most stable organic component of living things.

Naturally occurring alkane molecules contain from 1 to 40 or more carbon atoms. There are, exclusive of cycloalkanes nearly 10^{15} different structures of C_1 through C_{40} paraffins.[5] As noted above, biosyntheses are highly selective processes. If living things were a major source of sedimental alkanes, it may be expected that certain specifically structured hydrocarbons are present in natural mixtures of alkanes in high concentrations.

Although the identities of most naturally occurring C_{12} and larger paraffins have not been determined, structural similarities have been established between these compounds and other biological lipids.[6-9] Extensive research has shown that the acids and alcohols found in these lipids are constructed from acetate units.[10-15] Normally, the acetates combine either in a linear fashion to form straight chain compounds or into isoprenoid intermediates which join in turn to form terpenes or steroids. Mevalonic acid apparently is the principal precursor of isoprenoids, and the precise manner in which the isoprene building units combine to form many isoprenoids and steroids are known.[14]

Various methods are available for isolating linear compounds[16] and such compounds are easily identified. n-Paraffins are the most abundant alkanes in biological and sedimental lipids,[9] but the simplicity of the single carbon replicating CH_2 unit in n-paraffins is readily duplicated by abiotic reactions.[17] Therefore, the common presence of linear alkanes in organisms and sediments may not provide strong evidence of the biological origin of sedimental hydrocarbons.

When our original research proposal was submitted to NASA[18], no isoprenoid-type C_{12} or larger alkanes had been identified in natural samples, although the presence of these compounds in sediments and crude oils had been predicted.[7,18] It was hypothesized[18] that the common occurrence of precisely structured isoprenoids in sedimental and biological alkanes would confirm the biological origins of these compounds.

Now, seven isoprenoid-type alkanes have been identified in crude oils[19-22], and five of these terpanes have been isolated from oil shale extracts.[23] Concentrations of the individual terpanes ranged from 0.08 to greater than 1.0 per cent in the various natural samples. These concentrations are apparently millions of times greater than would be found for the same terpanes in a randomly produced mixture containing all the kinds of hydrocarbons that are in petroleum. The analyses of terpanes in crude oils and oil shale extracts afford strong evidence of the biological origin of these hydrocarbons.

Exploitation of paraffins in paleobiological and space investigations may be experimentally and theoretically defended. Much work, however, remains to be done before the full potential of alkanes in biological studies can be empirically established and fully determined. For example, only two of the isoprenoids identified in crude oils are known to appear in biological lipids[24-25]. Additional identifications and an assessment of factors controlling the compositions of sedimental hydrocarbons are needed to increase the legibility of the biologic records retained by alkanes in sediments.

Under NASw508, an effort is being made to devise simple methods of recognizing biological hydrocarbons and to determine their stabilities. Gas chromatographic "fingerprints" and mass spectra are being obtained of alkanes from living things, sediments, and a Fischer-Tropsch or abiotic product. Non-gradational changes in the concentrations of successive homologs appears to be a common and easily detected characteristic of biological hydrocarbons.[26] Alkanes from bat guano and a 60 million year old sediment, both, contain higher concentrations of even-than of odd-carbon number n-paraffins in the C_{11} to C_{20} range and higher concentrations of odd-than even-carbon number n-paraffins in the C_{23} to C_{33} range.[26] Fischer-Tropsch saturated hydrocarbons, on the other hand, show a systematic decrease in concentrations of homologous alkanes. These latter concentrational changes may be explained by the loss of volatile components from a product in which reaction equilibria led to a decrease in concentrations of the compounds with higher carbon numbers.[26]

Data, also, were collected which permitted a testing of the hypothesis that the biochemically and chemically least active biological molecules may accumulate unaltered in the elimination products and, then, in sediments.[27] Comparable concentrations of alkanes were found in the benzene extracts of cow manure, bat guano, and Recent sediments. These concentrations exceed by two orders of magnitude the concentrations of alkanes in extracts of butter and of plant and animal tissues.[27] Mass spectrometric and gas chromatographic analyses indicate that alkanes from various sedimental and biological sources contain the same types of compounds.[9,26,27]

Many analyses are being obtained of alkanes from a 1.1 billion year old crude oil. Optical activities of these paraffins are of the same sign and magnitude as are the optical activities of hydrocarbons from relatively young oils.[27] Pristane, 2, 6, 10, 14-tetramethylpentadecane, has been tentatively identified in the 1.1 billion year old oil. Gas chromatograms and mass spectra show a slightly greater abundance of odd- than of even-carbon number C_{21} through C_{33} n-paraffins in this oil.[28]

Compositely, data gathered on the ancient (None-Such) crude oil indicate a remarkable stability for biological alkanes in sediments. Pristane has been found in many biological lipids.[29] Its precise structure is difficult to duplicate by abiotic reactions.[30] Similarities have been observed in the distribution of optically active components of alkanes from kelp,[31] Recent sediments,[32] and crude oils.[33] The most optically active compounds in crude oils are apparently tetra- and pentacyclic hydrocarbons with molecular weights approximating those of parent steroid hydrocarbons.[33,34] n-Paraffins from some organisms display an odd carbon preference in the C_{21}-C_{33} range.[9,26]

Essentially all the structural units which comprise biological alkanes could be found in pristane, polycyclic alkanes, and n-paraffins. The compounds appear to be present in the None-Such oil as well as in younger oils and in living things. Geologic studies indicate that the None-Such oil is approximately 1.1 billion years old.[35] Thus optical, chromatographic, and spectrometric data suggest that alkanes in this ancient petroleum have not undergone significantly more alterations than have identical or similar hydrocarbons in 30 to 60 million year old crude oils.[8,26-28]

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